PCT/EP 98/06047

EPO - DG 1
EP 98/06047
07.01.1999

The Patent Office

The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP9 1RH

09/508512

PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN COMPLIANCE WITH RULE 17.1(a) OR (b)

EU,

REC'D 07 JAN 1999
WIPO PCT

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

3
1

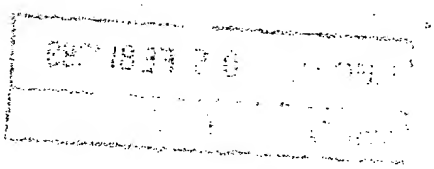
In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

Signed Andrew Gersey

Dated 1 October 1998



Patents Form 1/77

Patents Act 1977
(Rule 16)

The Patent Office

1/77

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

24 SEP 1997

The Patent Office
Cardiff Road
Newport
Gwent NP9 1RH

1.	Your reference	SCB/CDM/49207/000
2.	Patent application number *(The Patent Office will fill in this part)*	9720371.5 — 24 SEP 1997
3.	Full name, address and postcode of the or of each applicant *(underline all surnames)*	**EUROPEAN ATOMIC ENERGY COMMUNITY (EURATOM)** **Commission of the European Communities** **Bâtiment Jean Monnet** **Plateau du Kirchberg** **L-2920 LUXEMBOURG**
	Patents ADP number *(if you know it)*	4378049004
	If the applicant is a corporate body, give the country/state of its incorporation	**LUXEMBOURG**
4.	Title of the invention	**METHOD AND APPARATUS FOR SELECTIVELY MONITORING TRITIATED WATER VAPOUR IN A GAS**
5.	Name of your agent *(if you have one)*	**BOULT WADE TENNANT** **27 FURNIVAL STREET** **LONDON** **EC4A 1PQ**
	"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*	
	Patents ADP number *(if you know it)*	**42001**

6.	If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number	Country	Priority application number (if you know it)	Date of filing *(day/month/year)*

7.	If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	Number of earlier application	Date of filing *(day / month / year)*

8.	Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:* *a) any applicant named in part 3 is not an inventor, or* *b) there is an inventor who is not named as an applicant, or* *c) any named applicant is a corporate body.* *See note (d))*	YES

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form	
Description	**16**
Claim(s)	**7**
Abstract	
Drawing(s)	**2 + 2**

10. If you are also filing any of the following, state how many against each item.

Priority documents	
Translations of priority documents	
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
Request for preliminary examination and search *(Patents Form 9/77)*	
Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(Please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Signature

Date

24 September 1997

12. Name and daytime telephone number of person to contact in the United Kingdom

Colm D. Murphy
0171 404 5921

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents ct 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

a) *If you need help to fill in this form or you have any questions, please contact the Patent Office on 01645 500505.*

b) *Write your answers in capital letters using black ink or you may type them.*

c) *If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.*

d) *If you have answered 'Yes' Patents Form 7/77 will need to be filed.*

e) *Once you have filled in the form you must remember to sign and date it.*

f) *For details of the fee and ways to pay please contact the Patent Office.*

METHOD AND APPARATUS FOR SELECTIVELY MONITORING TRITIATED WATER VAPOUR IN A GAS

The present invention is concerned with a method and apparatus for selectively monitoring hydrophilic tritium-containing species in a gas, and in particular with such a method and apparatus which selectively monitors tritiated water vapour in the air of a controlled area for tritium handling.

Tritium is an isotope of hydrogen which undergoes radioactive decay by emission of a beta-particle. The most common forms of tritium encountered in air are the elemental form HT, DT or T2 (usually referred to generically as HT) and in the oxidised form HTO, DTO and T2O (usually referred to generically as HTO). The elemental form of tritium has a radiotoxicity 25000 times lower than the oxidised form, according the International Commission on Radiation Protection. This is because, whereas the oxidized form mixes thoroughly with the water in the lungs, the elemental form is hardly absorbed at all, and shows a slow rate of isotope exchange with the water in the body. Some scientists claim the absorption of HT has been somewhat underestimated, so that a HTO/HT radiotoxicity ratio of as low as 1000 is more appropriate.

Sometimes other tritiated molecules, such as tritiated hydrocarbons, methanol etc., may be present in the gas. Whilst no international standards exist for the radiotoxicities of these species, one would expect that they are proportional to the amount by which the species enter, or exchange tritium with, water in the lungs.

Clearly it is important to distinguish between the

chemical forms of tritium, especially between the most common forms; oxidized and elemental; because of the large difference in radiotoxicity.

Presently tritium is monitored either without discriminating between the two main chemical forms, by, for example, using ionisation chambers, internal gas-proportional counters, or scintillators of various kinds, such as anthracene, or the like; or by means of delayed methods that separate the humidity from the air, for example, by absorption in a bubbler, desiccation, condensation or freezing. The sample must then be subsequently measured by, for example, liquid scintillation counting or alternatively by one of the above methods.

For the measurement of tritium concentration in ambient air, the most widely and commonly used monitors are ionisation chambers.

A monitor, selective for tritiated water, which has been previously used is generally based on two ionisation chambers connected by a selectively permeable (Nafion-Dupont) membrane. Such a monitor has been developed so as to discriminate between HTO and HT concentrations in a gas. Such monitors suffer from the disadvantage that they have a limited discrimination factor due to the permeability of the membrane for both HTO and HT. Furthermore, they can experience a long delay caused by the time-period sufficient for the gas to penetrate the membrane. The system is also bulky and expensive.

Another existing HTO-selective monitor consists of two ionization chambers in series, separated by a drier. The HTO concentration is deduced by subtracting the signal emitted by the second ionization chamber from

that of the first ionization chamber. One disadvantage of this system is that, if HT is present in higher concentrations than HTO, the errors in the ionization chamber measurements may greatly exceed the HTO concentration. The system is also bulky and expensive.

Therefore it is an object of the present invention to provide a novel method and apparatus which may discriminate between the oxidised form of tritium and elemental form of tritium in a gas to provide a measure of tritium water vapour (HTO) in a gas.

Therefore, according to a first aspect of the present invention there is provided a hygroscopic scintillator, suitable for selective response to tritiated water vapour and other hydrophilic tritiated species in a gas, which scintillator comprises a solid scintillator material coated with a layer of hygroscopic material. Such a scintillator advantageously allows tritiated water vapour or other hydrophilic gas species, such as, for example, tritiated ammonia, tritiated methanol or the like to enter or exchange tritium, holding the tritium from said species in close proximity to the surface of the solid scintillator material.

The range of the beta-emission from tritium (average about 0.4 microns in liquid water) allows the tritium in the hygroscopic layer to excite the solid scintillator component of the hygroscopic scintillator element. Advantageously, the hygroscopic layer may consist of a layer of any hygroscopic or deliquescent substance such as a solution of deliquescent compound, or an aqueous gel of said compound. A hydrated solid or zeolite may also be used in the hygroscopic layer: these have the disadvantage of a relatively slow exchange rate of water with the water vapour in the

gas, but the advantage in some special applications of being selective only for tritiated water, and not other hydrophilic species.

The range of tritium beta-emissions being limited, only the surface region of the scintillator material of the scintillator element contributes to the monitor sensitivity. Therefore said scintillator material may advantageously be of a form with high specific surface area, for example as sheets, fibres, powder, powder compact, paint, varnish or a combination of the said forms.

There is provided by a second aspect of the present invention a method of monitoring tritiated water vapour activity in a gas, which method comprises contacting said gas with a scintillator according to the invention said scintillator being enclosed in a substantially light tight container, and measuring the light emitted from said hygroscopic scintillator, the amount of said light emitted from said scintillator providing a measure of the tritiated water activity of said gas.

Thus, advantageously, the method according to this aspect of the present invention discriminates between the oxidised form of tritium in a gas, and the elemental form of tritium, the oxidised form of tritium being highly radio-toxic compared to the elemental form of tritium.

Furthermore, during operation the hygroscopic scintillator element contains an amount of HTO typically contained in a volume of gas much larger than the volume of the monitor. Therefore, the method according to the first aspect of the present invention advantageously allows a much more compact format than

an ionization chamber sensitive to the same activity of HTO in gas.

Advantageously, the method according to this aspect of the present invention may have a sensitivity to all tritium-containing species in the gas, substantially in proportion to the amount by which they enter or exchange tritium with the water-containing layer in the hygroscopic scintillating element. Since the relative radiotoxicity of the tritiated species depends substantially on their entry and isotope-exchange with water in the human lung, one may expect the monitor to give a good indication of the overall radiotoxicity of the gas mixture due to all tritium species present.

Solid scintillators advantageously emit light when hit by a beta-emission from tritium, and, unlike liquid scintillation cocktails, have a stable geometrical form and negligible evaporation rates. Preferably, the scintillator according to the invention may be, for example, a plastic, a glass, an inorganic "phosphor" (e.g. doped zinc sulphide), an oxide-based material (e.g. Yttrium Aluminium Garnet "YAG" or Yttrium Aluminium Perovskite "YAP": crystalline oxides available in transparent single crystal form), or a combination of these materials. All these solid scintillator materials have been used before in various forms of radiation detectors. None absorb significant quantities of water.

Advantageously, to improve wetting, the solid scintillator material may be pre-treated on the surface with a detergent, or subjected to a hydrophilic surface treatment such as sulfonation or the like; or alternatively detergent may added to the aqueous component.

Preferably, a light guide of transparent material may be provided to help transmit light from the scintillator to the light detector(s). In some cases, the solid scintillator material itself may act as a light guide.

When measuring tritiated water vapour in a process gas, such as, air, the humidity of the air can affect the reading presumably in two ways. Firstly, for a given activity of tritiated water in the gas (in terms of Becquerel per cubic meter of gas), the concentration of tritium per gram of water is inversely proportional to the humidity of the gas. This effect tends to decrease the sensitivity of the monitor (in terms of Becquerel per cubic meter of gas) as the humidity increases. Secondly, the amount of water present in the hydrated layer increases with the humidity, depending on the absorption characteristics of the hygroscopic layer. This in turn tends to increase the amount of water contributing to the scintillation, and hence tends to increase the output of the monitor as humidity increases. Therefore, the two effects tend to cancel each other. Preferably, by optimizing the nature and thickness of the hygroscopic layer, the variation in sensitivity of the output with changing humidity in the gas can be minimized.

In a preferred embodiment of this aspect of the present invention, the light emitted by the hygroscopic scintillator element is measured by one or more photomultipliers, multichannel plates, or photodiodes or the like which would be well known to those skilled in the art. The electronics associated with such light detectors may use conventional current-pulse-counting, each pulse substantially corresponding to a light pulse from a scintillation event. As usual for scintillation techniques, the rate

of current pulses is substantially proportional to the rate of scintillation events. Where two or more light detectors are used, one may advantageously reduce noise background by well-known pulse coincidence detection techniques. If the light output is sufficient, continuous average-current monitoring may be used instead of pulse counting.

In one embodiment of this aspect of the present invention the gas to be monitored may be air. Thus, advantageously, the method may be used to monitor the tritium breathed, for example, by radiation workers in a controlled handling area. In a preferred embodiment the air tritium monitor may be small enough to be carried continuously by workers in a controlled area.

In another embodiment of this aspect of the present invention, the gas to be monitored may be enclosed in a chemical plant: an application normally described as a "process monitor". In a light-tight plant, the monitor may be inserted through the plant wall (for example into a pipe or storage tank) without the need of its own light-tight container.

Preferably, such a process monitor may be used in conjunction with a non-discriminating monitor in order to measure, by difference, the concentrations in gas or air of both tritiated water (possibly together with hydrophilic species) and elemental tritium (possibly together with other hydrophobic species). In this embodiment, the non-discriminating tritium monitor may be substantially identical to the discriminating monitor with the exception that the hygroscopic layer is omitted in the non-discriminating monitor.

Preferably, a second radiation monitor; preferably substantially identical to the said discriminating

monitor, but sealed in a container free of radioactive gas, may be used to compensate for background radiation fields (e.g. gamma-radiation), by subtraction: an analogous technique is already used for compensating ionization chambers for radiation background.

According to a further aspect of the invention there is provided **apparatus** for monitoring the level of tritiated water and other tritiated hydrophilic species in a gas, which apparatus comprises: a hygroscopic scintillator according to the invention, means for contacting said gas with said hygroscopic scintillator, and means for measuring the amount of light emitted from said hygroscopic scintillator element.

Thus, advantageously, the apparatus according to this aspect of the invention provides a measure of the level of tritium in a gas, such as for example, air. The apparatus responds with much greater sensitivity to tritiated species, such as tritiated water vapour, which are more radiotoxic because they mix or exchange hydrogen isotopes rapidly with water.

This further aspect of the present invention may be in the form of a stand-alone room air monitor, a personal tritium monitor or an "in-line" process gas monitor for mounting with tube connectors in the pipework of a chemical process using tritiated gas. In these two embodiments, the hygroscopic scintillator may be enclosed in a light-tight container with a window(s) or aperture(s) to allow light to reach the light detector(s), an inlet and outlet to allow flow of said gas or air over or through the hygroscopic scintillator element. Preferably, said inlet and outlet should minimize the entry of external light by,

for example, the use of dark or black materials and have a geometry which forces the light to make multiple reflections before reaching the monitor.

For a stand-alone room air monitor, a pump is preferably provided to pass air continuously through the monitor. Furthermore, a dust filter may be mounted at the inlet. When the apparatus is used as a personal tritium monitor, a pump may be provided, or the monitor may be built into a breathing mask so that the flow of air is provided by the breathing of the worker. Furthermore, when used as a process gas monitor, a pump may be used to pass gas there through if the gas flow or pressure drop available inside the plant is insufficient. Such an application could be, for example, the monitoring of tritium in an inert-gas glovebox. The pump for the two embodiments described herein may be of many types, for example, including a membrane pump, an electrical fan or impeller, a centrifugal pump or advantageously (for reason of low power consumption) a piezo-electric fan built into a housing. Thus advantageously the apparatus according to the invention may provide a substantially continuous monitoring of the tritium radiotoxicity in a gas.

The apparatus may also be provided in the form of a "nude" monitor for process gas in an existing light-tight tank or pipe. Lacking its own light-tight casing, the apparatus according to the invention may be fixed to an aperture in the plant wall or pipe with a substantially light-tight seal. In this embodiment, gas flow through or over the hygroscopic scintillator element may be provided by the existing flows inside the plant, or alternatively a fan.

Advantageously, the apparatus according to the present

invention uses a hygroscopic layer coated onto a solid scintillator to make a hygroscopic scintillating element. Said hygroscopic layer may consist of a layer of hygroscopic or deliquescent substance such as a solution of deliquescent compound, or an aqueous gel of said compound. Many compounds are suitable: examples are zinc chloride, potassium acetate, phosphoric acid, lithium chloride. The use of a gel containing deliquescent compound may advantageously impede long-term redistribution of the hygroscopic layer across the surface. A hydrated solid such as for example zeolite may also be used in said hygroscopic layer: this has the disadvantage of a relatively slow exchange rate of water with the water vapour in the gas, but the advantage in some special applications of being selective only for tritiated water, and not other hydrophilic species.

The solid scintillator material, or a combination of solid scintillator materials, may advantageously be applied as a paint (e.g. zinc sulphide paint) or varnish (e.g. plastic scintillator dissolved in organic solvent, possibly mixed with YAP powder) to the surface of the light guide. The advantages are a reduction in cost of scintillator material, efficient light collection, and relative insensitivity to gamma radiation, due to the small mass of solid scintillator present. In other foreseen designs, using a transparent solid scintillator, the latter may combine the function of a light guide.

In the apparatus according to the invention, the inside walls of the light-tight container, or the surface of a light guide, may preferably be made reflective, for example by polishing or aluminizing, to improve light collection efficiency.

The apparatus according to the invention has a certain sensitivity to HT and other hydrophobic tritiated species due to the arrival at the scintillator of tritium beta emissions arising from such species in the gas in and around the scintillator element, the range of tritium emissions in gas being much greater than in condensed phases. This sensitivity to HT is approximately proportional to the volume of gas in and around the scintillator element. It is possible to vary the relative sensitivity to HT, for a given HTO sensitivity, by keeping the same surface area and preparation method for the hygroscopic scintillator element, but varying its overall size to change the gas space inside the scintillating element. Alternatively, extra scintillator material may be added, not covered by a hygroscopic layer. Thus the ratio of HTO to HT sensitivity may be adjusted to match a desired value, for example 1000.

Preferably, the light emitted by the hygroscopic scintillator element is measured by one or more photomultipliers, multichannel plates with photodiode detectors, or photodiodes. The electronics associated with such light detectors may use conventional current-pulse-counting, each pulse substantially corresponding to light pulse from a scintillation event. As usual for scintillation techniques, the rate of current pulses is substantially proportional to the rate of scintillation events. Where two or more light detectors are used, one may advantageously reduce noise background by well-known pulse coincidence detection techniques. If the light output is sufficient, continuous average-current monitoring may be used instead of pulse counting.

Preferably, there is provided electronics to convert the rate of charge pulses or average current into a

signal which is substantially proportional to the radiotoxicity of the gas, or its logarithm. Said signal may preferably be displayed on a meter or digital display, and/or made available as an output to a computer, data-logger or other external recording or control apparatus. A standard humidity gauge may be incorporated into the monitor, or a separate humidity gauge may be read into said recording and control apparatus, in order to allow automated or manual compensation for the effects of gas or air humidity on the sensitivity of the present tritium monitor. Furthermore, it is foreseen that the function of said humidity gauge may be incorporated into the monitor by measuring the electrical AC or DC conductivity of the hygroscopic layer, for example by measuring the resistance between two metallic contacts applied to the surface of the solid scintillator before coating with the hygroscopic layer.

The invention may be more clearly understood by the following description of an embodiment thereof, with reference to the accompanying drawing given by way of example only, wherein Figure 1 illustrates apparatus for monitoring the tritiated water content, or more generally radiotoxicity of a gas containing tritium species, according to the invention. The electronics are not shown, not being innovative. Figures 2 to 6 illustrate alternative embodiments of the apparatus of Figure 1. In each figure there is shown one or more light detectors indicated by the reference numeral 1, and a hygroscopic scintillator element 2, Some designs have a light guide 3 of non-scintillating transparent material.

Fig.1 is an illustration of apparatus according to the invention. There is shown a simple design for the monitor 1, where gas 2 passes over one surface of a

flat hygroscopic scintillator element 3, which can be supported by a backing plate. There is no light guide: the scintillation light pulses pass through the sample gas 2 being introduced to reach the light detector 4. This design is particularly suitable for fragile scintillator elements: powder compacts and the like; and for layers of substantially opaque and non-porous solid scintillator, such as paints of inorganic phosphors (e.g. doped zinc sulphide paint).

Fig.2 illustrates a monitor 5 of similar geometry to the monitor of fig. 1 except that the gas 6 passes through a porous hygroscopic scintillator element 7, for example a porous powder compact supported on a filter 8. In this case, the amount of hygroscopic material applied to the powder compact should be limited, not to block the passage of the test gas.

Fig. 3 illustrates a monitor 10 of a simple geometry with high light collection efficiency, made by coating a thin layer of solid scintillator 11 coated onto the face of a light guide 12, before applying the hygroscopic layer. Even more simply, one may eliminate the light guide, applying the solid scintillator directly onto the face of the light detector.

Fig.4 illustrates a monitor 20 comprising parallel sheets of solid scintillator (e.g. plastic, glass, scintillating crystal), coated with the hygroscopic layer, and glued (using transparent glue) inside a channel 22 traversing a block of transparent material 23 which acts as a light guide. The same overall geometry may be realized by making the sheets mostly of the light-guide material, and then coating them with a layer of solid scintillator, before applying the hygroscopic layer.

The overall geometry shown in fig.4 can alternatively be obtained by making it from a single block of transparent plastic or resin: e.g. by injection moulding. The surfaces of the parallel plates are then coated first with a solid scintillator and then with a hygroscopic layer.

In monitor 30 illustrated in figure 5, solid scintillator fibres 31 are coated with the hygroscopic layer and held in a tube 32: the fibres themselves acting as light guides. The same geometry can be obtained by first coating non-scintillating transparent fibres with a layer of solid scintillator.

Figure 6 illustrates a monitor 40 of a single light-detector design with a spiral of hygroscopically-coated plastic scintillator sheet 41 glued onto the end-plate of the light guide 42, which forces the gas to spiral inwards towards the central outlet tube (reverse flow is also possible). Fig.7 shows a similar hygroscopically coated scintillator element, this time with axial gas flow and no light guide.

Figures 4,5 and 7 show double light detectors, to enable background noise reduction by coincidence detection. In each case, one of the two detectors can be replaced by a reflector if pulse coincidence detection is not desired. Conversely, in the other designs, two light detectors may be used instead of one to allow pulse coincidence detection: they can both view the same side of the hygroscopic scintillator element where it is not advantageous to mount the detectors on opposite sides (e.g. if the scintillator is opaque).

Prototype monitors and initial results

To be of use, the monitor must have a limit-of-